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## Optics Communications

journal homepage: [www.elsevier.com/locate/optcom](http://www.elsevier.com/locate/optcom)Spectral-kinetic studies of SrAlF<sub>5</sub> doped by trivalent rare-earth ions

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## ABSTRACT

Photochemical properties of Ce<sup>3+</sup>:SrAlF<sub>5</sub> and Ce<sup>3+</sup>,Yb<sup>3+</sup>:SrAlF<sub>5</sub> single crystals together with spectroscopic and kinetic characteristics of several optically nonequivalent impurity centers and energy transfer between them are described. It is shown that co-activation by Yb<sup>3+</sup> ions effectively suppresses color centers in Ce,Yb:SAF crystals. It was found out that in Ce,Yb:SAF crystals Yb ions exist simultaneously in 2+ and 3+ valent state. Three types of optically nonequivalent luminescent centers corresponding to the doublets in luminescence spectrum centered at 290, 305 and 370 nm (Ce<sup>I</sup>, Ce<sup>II</sup>, Ce<sup>III</sup>, respectively) have been observed. Analysis of luminescence spectra and decays leads to the conclusion that there is no energy transfer between either cerium centers or from Ce<sup>3+</sup> to Yb<sup>2+</sup> apart from the Ce<sup>III</sup> center which luminescence is slightly quenched by Yb<sup>2+</sup>.

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## 1. Introduction

Searching for and investigating new perspective active media for UV tunable solid state lasers is an urgent task, because modern technology requires as short wavelength of laser emission as possible [1]. SrAlF<sub>5</sub> (SAF) crystals doped by rare-earth (RE) ions, especially Ce<sup>3+</sup> [2], is a very promising laser material for the UV/VUV spectral ranges due to broad band-gap (12.3 eV [3,4]) and chemical composition similar to the most effective UV laser active media LiCaAlF<sub>5</sub> and LiSrAlF<sub>5</sub>. SAF crystals doped by iron-group ions are known as rather effective IR laser material [7]. It could also be doped by RE<sup>3+</sup> ions and despite their rather low segregation coefficient it is still enough for practical applications in quantum electronics devices based on interconfigurational transitions of active ions.

Because of Goldschmidt's rule trivalent RE<sup>3+</sup> ions dominantly substitute for divalent strontium lattice cations which in this crystal exist in four nonequivalent positions [8]. Besides charge compensation is required. Thus several optically nonequivalent RE<sup>3+</sup> centers formation are expected. Presence of the few types of optically nonequivalent active centers in one medium especially if the energy exchange between them is ineffective will inevitably lead to the dissipation of excitation energy and puts into question the use of this material for laser applications [9].

In literature there are a lot of contradictory assignments of the SrAlF<sub>5</sub> crystalline space group [5,6]. According to the most common viewpoint this crystal belongs to the noncentrosymmetric space group *I4* and there are a lot of studies in favor of

ferroelectric effect existence in this material [5]. In such case active medium with controllable spectral properties is the one of interest. But on the other hand more recent theoretical and experimental studies report centrosymmetric space group *I4<sub>1</sub>/a* for SrAlF<sub>5</sub> which eliminates any ferroelectric behavior [6]. Therefore optical and spectroscopic properties studies of this crystal still remain an urgent task.

Another problem in the way of the search for the new materials for UV laser applications is that the most fluoride crystal hosts are subjected to the strong coloration under pumping condition (for example, [10]). To level this effect coactivation with Yb<sup>3+</sup> ions has been successfully applied before [10]. The disadvantage of such approach are that: (a) doping by RE<sup>3+</sup> ions generally leads to the formation of crystal lattice defects serving as the nuclei for color centers formation; and (b) Ce<sup>3+</sup> ions 5d–4f luminescence could be significantly quenched by ytterbium ions, thus optimization of activator ions concentrations should be performed.

This paper reports on spectral, kinetic and photochemical properties of Ce:SAF and Ce,Yb:SAF single crystals of several optically nonequivalent RE impurity centers and energy transfer between them.

## 2. Experimental details

The tetragonal Ce:SAF and Ce,Yb:SAF crystals with doping concentration ~0.5 at% in the melt were grown in Ar-atmosphere in carbon crucibles using Bridgman–Stockbarger technique. The melt contained a slight excess of AlF<sub>3</sub> above the stoichiometric composition. High-purity chemicals (>99.99%) of commercially available SrF<sub>2</sub>, AlF<sub>3</sub>, CeF<sub>3</sub>, and YbF<sub>3</sub> powders were

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